

## DESCRIPTION

### Laminated Zeolite Composite and Method for Preparation Thereof

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#### Technical Field

The present invention relates to a laminated zeolite composite and a method for producing the laminated zeolite composite.

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#### Background Art

Zeolite composite membranes obtained by forming a zeolite membrane on a substrate have been known and have been used as a gas separation membrane or a liquid separation  
15 membrane. With respect to such zeolite composite membranes, it is known that when the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of the membrane (hereinafter, it means a molar ratio when simply " $\text{SiO}_2/\text{Al}_2\text{O}_3$ " is mentioned) varies, the interaction between the pore surface of zeolite and a molecule passing therethrough  
20 varies and the characteristic of the membrane when used as a separation membrane varies as well.

In, for example, p. 25 of an article by Yoji Sano and Yushi Kawakami in Kagaku Kogyo, Feb. 1995 is disclosed a finding on the influence of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  on the permeation and  
25 separation characteristic of MFI type zeolite membrane (hereinafter referred to also as "MFI membrane") when water and alcohol are separated from each other by pervaporation using the membrane. It is known that the membrane shows striking alcohol selectivity when the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  thereof is  
30 increased.

As a specific example of the generally used MFI membrane, there can be mentioned a zeolite composite membrane obtained by forming a MFI membrane on an alumina substrate. With respect to such a zeolite composite membrane, it is known that, during the formation of the MFI membrane, aluminum in the alumina-made substrate dissolves into the MFI membrane and is taken into the skeleton of the MFI membrane and, as a result, the MFI membrane becomes a  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -reduced MFI membrane (hereinafter this membrane is expressed also as "low-silica MFI membrane").

Also in JP-A-6-127937 are disclosed a self-supported MFI membrane not formed on any substrate (hereinafter this membrane is expressed also as "MFI self-supported membrane"), into which aluminum is taken and wherein the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  is reduced; and a method for production thereof.

In the zeolite composite membrane obtained by forming a MFI membrane on an alumina substrate, however, it is impossible to control the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the MFI membrane strictly and, therefore, it is difficult to steadily synthesize a low-silica MFI membrane exhibiting uniform separation characteristic. Further, in synthesis of the MFI membrane, a structure-directing agent is added generally and it is necessary to remove the structure-directing agent by high-temperature calcination; however, since the substrate alumina and the MFI membrane (zeolite) differ in thermal expansion coefficient, the MFI membrane may generate cracks during calcination.

In the zeolite membrane described in JP-A-6-127937, since it is a MFI self-supported membrane, there can be avoided problems such as crack generation in MFI membrane due

to difference in thermal expansion coefficient between substrate and zeolite. Even in the method for production of MFI membrane according to the above literature, however, it is described therein that the MFI membrane formed at the  
5 initial stage of synthesis has a large  $\text{SiO}_2/\text{Al}_2\text{O}_3$ , and the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  tends to become smaller with the growth of the membrane; therefore, a low-silica MFI membrane having small value in  $\text{SiO}_2/\text{Al}_2\text{O}_3$  is obtainable only when the thickness of the membrane is made large. Consequently, the MFI membrane  
10 obtained exhibits permeation and separation characteristic as a low-silica MFI membrane, but has a large thickness and accordingly a small permeation factor and has a problem of low permeability.

The present invention has been made in view of such  
15 problems possessed by the prior art, and aims at providing a laminated zeolite composite having high separation characteristic and high permeability, and a method for producing such a laminated zeolite composite.

## 20 Disclosure of the Invention

According to the present invention, there is provided a laminated zeolite composite characterized in that it comprises a MFI membrane being constituted by a MFI type zeolite and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 40 to 100,  
25 and a porous substrate being constituted by a MFI type zeolite and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 20 to 400, and that the MFI membrane is formed on the porous substrate.

In the present invention, the MFI membrane has a thickness of preferably 25  $\mu\text{m}$  or less. Incidentally, the  
30  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of the MFI membrane may gradually

decrease from the side of the membrane contacting the porous substrate toward other side thereof.

The laminated zeolite composite of the present invention is suitably used for separation of butane isomers  
5 or separation of propane and propylene.

According to the present invention, there is also provided a method for producing a laminated zeolite composite comprising immersing a porous substrate in a silica sol-  
containing sol for membrane formation, and forming a MFI  
10 membrane on the porous substrate under heating conditions; said method being characterized in that a porous substrate being constituted by a MFI type zeolite and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 20 to 400 is immersed in a sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 40 to  
15 150 and a  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  (molar ratio) of 15 or less.

In the present invention, it is preferred to form a MFI membrane being constituted by a MFI type zeolite and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 40 to 100.

## 20 Brief Description of the Drawings

Fig. 1 is a schematic drawing showing a mode for carrying out the permeation and separation test of butane isomers. Fig. 2 is a graph wherein the separation factor of butane isomers is plotted against the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of MFI  
25 membrane.

## Best Mode for Carrying Out the Invention

Modes for carrying out the present invention are described below. However, the present invention is not  
30 restricted to the following modes and it should be construed

that design change, improvement, etc. may be made appropriately based on the ordinary knowledge of those skilled in the art as long as there is no deviation from the gist of the present invention.

5           The first aspect of the present invention lies in a laminated zeolite composite characterized in that it comprises a MFI membrane being constituted by a MFI type zeolite and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 40 to 100, and a porous substrate being constituted by a MFI type  
10 zeolite and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 20 to 400, and that the MFI membrane is formed on the porous substrate.

          In the laminated zeolite composite of the present invention, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the MFI membrane may gradually decrease from the side of the MFI membrane contacting with  
15 the porous substrate toward other side of the MFI membrane. Incidentally, "gradually decrease" refers to that the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  decreases gradually within a range of 40 to 100. The details of the first aspect are described below.

          The present invention has been completed based on a  
20 finding that there is a correlation between the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of MFI membrane and the separation factor of butane isomers when the MFI membrane is used. That is, the laminated zeolite composite of the present invention obtained by forming a MFI membrane having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40 to 100, on a porous  
25 substrate being composed of a MFI type zeolite and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 20 to 400, has a characteristic of gas separation, for example, separation of butane isomers.

          In the above-mentioned p. 25 of an article by Yoji Sano and Yushi Kawakami in Kagaku Kogyo, Feb. 1995 is disclosed  
30 the influence of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of MFI membrane on the

permeation and separation characteristic of the MFI membrane in separation of water and alcohol, i.e. components separation when the to-be-treated material is a liquid; however, no mention is made therein on the influence on the gas separation characteristic when the to-be-treated material is a gas. The correlation between the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of MFI membrane and the characteristic of gas separation including separation of butane isomers has been found for the first time in the present invention.

Further, in the laminated zeolite composite of the present invention, since there is formed, on a porous substrate composed of a zeolite, a membrane (MFI membrane) composed of the same zeolite as in the porous substrate, there are avoided, during production or use of the composite, inconveniences such as crack generation in MFI membrane due to difference in thermal expansion coefficient between the porous substrate and the MFI membrane, and the MFI membrane keeps its function at a satisfactory level.

Incidentally, " $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio)" referred to in the present invention is a value obtained by measurement using energy dispersive spectroscopy (EDS).

A MFI membrane having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of below 40 is not preferred because the MFI membrane tends to generate cracks on the surface. Meanwhile, a MFI membrane having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of beyond 100 is not preferred because the MFI membrane, when used as a separation membrane, hardly exhibits its unique gas separation characteristic. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the MFI membrane is preferably 45 to 90, more preferably 50 to 80 from the standpoint of superior performance as a separation membrane. In order to allow the MFI membrane to have a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40

to 100, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the porous substrate is preferably 20 to 400. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the porous substrate is more preferably 40 to 100 which is the same level as in the MFI membrane.

5           In the laminated zeolite composite of the present invention, the MFI membrane preferably has a thin thickness of 25  $\mu\text{m}$  or less, whereby the MFI membrane has high separation characteristic and excellent permeability. In order for the MFI membrane to exhibit particularly excellent  
10 permeability, the thickness of the MFI membrane is preferably 17  $\mu\text{m}$  or less, more preferably 13  $\mu\text{m}$  or less. In the present invention, there is no restriction as to the lower limit of the thickness of the MFI membrane; however, the lower limit is sufficient at 0.1  $\mu\text{m}$  or more in view of, for example, the  
15 function the MFI membrane when used as a separation membrane and the practical producibility of the MFI membrane.

As the shape of the laminated zeolite composite of the present invention, there can be mentioned, for example, a bar shape, a pellet shape, a flat sheet shape, a tube shape, a  
20 monolithic shape and a honeycomb shape.

The laminated zeolite composite of the present invention, by utilizing its advantages of excellent separation characteristic and permeability and the property of hardly generating cracks, etc., can be suitably used as a  
25 separation membrane for carrying out separation of butane isomers or separation of propane and propylene.

Next, description is made on the second aspect of the present invention. The second aspect of the present invention lies in a method for producing a laminated zeolite  
30 composite comprising immersing a porous substrate in a silica

sol-containing sol for membrane formation, and forming a MFI membrane on the porous substrate under heating conditions; and said method is characterized in that a porous substrate being constituted by a MFI type zeolite and having a

5  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 20 to 400 is immersed in a sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) of 40 to 150 and a  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  (molar ratio) of 15 or less. In the present invention, it is preferred that a MFI membrane being constituted by a MFI type zeolite and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of

10 40 to 100 is formed. The details of the second aspect are described below. Incidentally, when simply " $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ " is mentioned hereinafter, it means a molar ratio.

When there is used a sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of below 40 or beyond 150, the MFI membrane

15 obtained is unable to have a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40 to 100. Even when there is used a sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40 to 150 but when the sol has a  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of beyond 15, there is formed a MFI membrane having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of below 40, which is not preferred.

20 In order for the MFI membrane formed to reliably have a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40 to 100, it is preferred to use a sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 50 to 130 and is more preferred to use a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 55 to 120. It is also preferred to use a sol for membrane formation having a

25  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of 13 or less and is more preferred to use a sol for membrane formation having a  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of 10 or less. Incidentally, there is no particular restriction as to the lower limit of the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of the sol for membrane formation used in the present invention; however, the lower

30 limit may be 1 or more in view of, for example, the practical



production conditions of laminated zeolite composite.

In the present invention, a porous substrate having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 20 to 400 is immersed in the sol for membrane formation. As the method for producing such a porous  
5 substrate, a known conventional method may be used. In an example, tetrapropylammonium hydroxide (TPAOH), a silica sol,  $\text{NaAlO}_2$ , etc. are mixed at desired  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and TPAOH/ $\text{SiO}_2$  (molar ratio); the resulting mixture is stirred and kneaded with heating, to vaporize water to obtain a dry gel; the dry  
10 gel is ground to obtain a powder; the powder is formed by an appropriate forming method to obtain a formed article; then, the formed article is subjected to, for example, a reaction under a steam pressure, whereby a porous substrate having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of desired range can be produced. Incidentally, as  
15 the appropriate forming method, there may be used an ordinary ceramic forming method such as extrusion forming, CIP forming, slip casting or the like.

In the above example of the production method of porous substrate, it is preferred to use  $\text{NaAlO}_2$  as a Na and Al  
20 source. When the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  is larger than 1, the porous substrate obtained has crystalline Na separated thereon; when the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  is smaller than 1, the porous substrate obtained has a small strength.  $\text{NaAlO}_2$  is preferred because it contains Na and Al at 1:1 (molar ratio) and the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$   
25 can be controlled strictly at 1.

The porous substrate produced by, for example, the above method is immersed in the sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40 to 150 and a  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of 15 or less; a reaction is allowed to take place under a heating  
30 condition; thereby, a MFI membrane is formed on the porous

substrate. Here, "under a heating condition" refers to a reaction in a temperature range of 100 to 200°C in a pressure vessel.

The obtained membrane-formed substrate is heated  
5 appropriately to at about 500 to 600°C in, for example, an electric oven and kept it for about 4 to 10 hours at this temperature to remove the structure-directing agent (TPA) used. The keeping time and the rate of temperature increase or decrease are determined appropriately so as to match the  
10 sizes of membrane-formed substrate and electric oven. Incidentally, in the present invention, the thickness of the MFI membrane formed is preferably set at 25 μm or less, more preferably at 17 μm or less, particularly preferably at 13 μm or less. Thereby, a laminated zeolite composite having high  
15 permeability can be obtained.

Incidentally, the thickness of the MFI membrane can be controlled by, for example, controlling the reaction time.

In the present invention, there is no restriction as to the lower limit of the thickness of the MFI membrane formed.  
20 However, the lower limit is sufficient at 0.1 μm or more in view of, for example, the function of MFI membrane as a separation membrane and the practical producibility of MFI membrane.

In the present invention, it is preferred to form a MFI  
25 membrane having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40 to 100 because the MFI membrane can allow the resulting laminated zeolite composite to have a particularly excellent function as a separation membrane. In order for the MFI membrane to exhibit a particularly excellent function as a separation membrane, the  
30 MFI membrane is more preferred to have a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of

45 to 90 and is particularly preferred to have a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 50 to 80.

### Examples

5           The present invention is specifically described below by way of Examples. However, the present invention is not restricted to these Examples.

(Examples 1 to 2 and Comparative Examples 1 to 6)

#### 1. Production method of porous substrate A

10           To 16.27 g of a 10% aqueous TPAOH solution (a product of Wako Pure Chemical Industries, Ltd.) were added 0.656 g of  $\text{NaAlO}_2$  (a product of Wako Pure Chemical Industries, Ltd.) and 40.05 g of about 30wt% silica sol (Snowtex S, a product of Nissan Chemical Industries, Ltd.). The mixture was stirred  
15 at room temperature for 1 hour using a desk shaker and then stirred and kneaded with heating at about  $80^\circ\text{C}$  using a hot stirrer, to vaporize water, whereby a colorless dry gel was obtained.

          The dry gel was ground to obtain a powder, after which  
20 the powder was subjected to uniaxial pressing with a die at a total pressure of 2 ton to obtain a formed article having a disc shape having a diameter of 19 mm and a thickness of 2 mm. The formed article was set on a fluororesin plate in a stainless steel-made pressure vessel with a fluororesin-made  
25 inner cylindrical container placing distilled water of the same weight as the formed article, in a state that there is no contact between the formed article and the water. After the pressure vessel was placed in an oven of  $180^\circ\text{C}$ , the contents of the vessel was subjected to a reaction under a  
30 self steam pressure for 12 hours, whereby a porous substrate

(porous substrate A) was obtained.

The crystal phase of the porous substrate A obtained was examined by X-ray diffractionmetry. As a result, the porous substrate A was found to be an MFI type zeolite of perfect crystal. Incidentally, as to the crystal phase of zeolite, a case when, in X-ray diffractionmetry, there was only a broad halo and no clear peak were found, in a region of 20 to 30° ( $\text{CuK}\alpha$ ), was expressed as "amorphous"; a case when a zeolite peak was seen even slightly, was expressed as "under crystallization"; and a case when all sharp peaks of zeolite were seen clearly and there was no halo, was expressed as "perfect crystal". Incidentally, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the porous substrate A was 50.

## 2. Production method of porous substrate B

To 16.27 g of a 10% aqueous TPAOH solution (a product of Wako Pure Chemical Industries, Ltd.) was added 40.05 g of about 30wt% silica sol (Snowtex S, a product of Nissan Chemical Industries, Ltd.). The mixture was stirred at room temperature for 1 hour using a desk shaker and then stirred and kneaded with heating at about 80°C using a hot stirrer, to vaporize water, whereby a colorless dry gel was obtained. The later operation was conducted in the same manner as in production of the porous substrate A, to obtain a porous substrate (porous substrate B).

The crystal phase of the porous substrate B obtained was examined by X-ray diffractionmetry. As a result, the porous substrate B was found to be an MFI type zeolite of perfect crystal. Incidentally, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the porous substrate B was 500 or more.

## 3. Formation of MFI membranes

There were mixed, so as to give compositions shown in Table 1, various raw materials, i.e. a 10% aqueous TPAOH solution (a product of Wako Pure Chemical Industries, Ltd.), distilled water, tetrapropylammonium bromide (a product of Wako Pure Chemical Industries, Ltd.), aluminum sulfate (14 to 18 hydrates) (a product of Wako Pure Chemical Industries, Ltd.), a 30wt% silica sol (Snowtex S, a product of Nissan Chemical Industries, Ltd.) and a 4N aqueous sodium hydroxide solution (a product of Wako Pure Chemical Industries, Ltd.). The mixture was stirred at room temperature for 60 minutes using a desk shaker to produce a sol for membrane formation. The sol for membrane formation was placed in a 100ml-stainless steel-made pressure vessel with a fluororesin-made inner cylindrical container. Therein was immersed the above-produced porous substrate A or B. After the pressure vessel was placed in an oven of 180°C, the contents of the vessel was subjected to reaction for 8 hours, whereby a MFI membrane was formed on the porous substrate. The resulting membrane-formed substrate was placed in an electric oven, the substrate temperature was elevated to 550°C and then kept it at this temperature for 4 hours to remove the TPA, whereby laminated zeolite composites were produced (Examples 1 to 2 and Comparative Examples 1 to 6).

Incidentally, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of each sol for membrane formation and the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of each porous substrate are shown in Table 2.

Table 1

	10% tetrapropylammonium hydroxide solution (g)	Distilled water (g)	Tetrapropyl ammonium oxide (g)	Aluminum sulfate (g)	30wt% silica sol (g)	4N aqueous sodiumhydroxi de solution (g)	Porous substrate
Exam. 1	15.26	49.85	0	0.21	6	1	A
Exam. 2	15.26	49.85	0	0.21	6	2	A
Comp.Exam. 1	15.26	49.85	1.995	0	6	0	B
Comp.Exam. 2	15.26	49.85	0	0.21	6	1	B
Comp.Exam. 3	15.26	49.85	0	0.21	6	3	B
Comp.Exam. 4	10.17	49.85	1.995	0.21	6	1.6	B
Comp.Exam. 5	15.26	49.85	1.995	0	6	0	A
Comp.Exam. 6	15.26	49.85	0	0.21	6	3	A

Table 2

	Sol for membrane formation		SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar ratio) of porous substrate
	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar ratio)	Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> (molar ratio)	
Exam.1	40 to 150	<15	50
Exam.2	40 to 150	<15	50
Comp.Exam.1	>150	-	>500
Comp.Exam.2	40 to 150	<15	>500
Comp.Exam.3	40 to 150	>15	>500
Comp.Exam.4	40 to 150	<15	>500
Comp.Exam.5	>150	-	50
Comp.Exam.6	40 to 150	>15	50

(Evaluation of MFI membranes (separation membranes))

- 5 1. Thickness measurement and surface observation of each MFI membrane

By observing the cross section and surface of each MFI membrane using a SEM, the thickness of each MFI membrane was measured and the generation of cracks at the surface of each MFI membrane was examined. A case when cracks were confirmed by the SEM observation, was rated as "present", and a case when no cracks were confirmed, was rated as "not present".

The thickness of each MFI membrane formed on each laminated zeolite composite was 15 to 25  $\mu\text{m}$ . The result of examination of the generation of cracks at the surface of each MFI membrane is shown in Table 3.

3. Permeation and separation test

A permeation and separation test for butane isomers was carried out by the Wicke-Kallenbach method. Fig. 1 schematically shows a mode for carrying out the permeation and separation test for butane isomers. Fig. 1 shows a state in which there is placed, inside a permeation and separation test apparatus 10, a separated gas-holding unit 12 fitted

with a laminated zeolite composite 11. Incidentally, the permeation and separation test apparatus 10 is heatable by an electric oven 13.

A mixed gas containing about 5% by volume of isobutane and about 5% by volume of normal butane (n-butane) was fed to one side of the laminated zeolite composite 11 using a N<sub>2</sub> gas as a carrier gas, under a heating condition of 200°C, and the gas after permeation, at the opposite side of the laminated zeolite composite was swept by a N<sub>2</sub> gas and analyzed by gas chromatography. The separation factor of butane isomers is shown in Table 3. Incidentally, the separation factor of butane isomers is a value determined by the following expression (1), wherein X<sub>n</sub> and X<sub>iso</sub> are, respectively, the molar concentrations of n-butane and isobutane at the supply side of the gas, and Y<sub>n</sub> and Y<sub>iso</sub> are, respectively, the molar concentrations of n-butane and isobutane at the permeation side of the permeated gas.

$$\text{Separation factor of butane isomers} = (Y_n/Y_{iso})/(X_n/X_{iso}) \quad (1)$$

Table 3

	Crack generation at surface of MFI membrane	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (molar ratio) of MFI membrane	Separation factor of butane isomers
Exam.1	Not present	52	84.3
Exam.2	Not present	79	62.0
Comp.Exam.1	Not present	225	16.0
Comp.Exam.2	Not present	130	16.3
Comp.Exam.3	Present	26	19.8
Comp.Exam.4	Not present	107	14.2
Comp.Exam.5	Not present	201	11.7
Comp.Exam.6	Present	29	14.2



In Fig. 3 is shown a graph in which the separation factor butane isomers are plotted against the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  value of each MFI membrane.

(Discussion)

5           In order to produce a laminated zeolite composite exhibiting excellent separation characteristic, it is required that (1) the porous substrate used has a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 20 to 400, (2) the sol used for membrane formation has a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40 to 150, and (3) the sol used for membrane  
10 formation has a  $\text{NaO}_2/\text{Al}_2\text{O}_3$  of 15 or less. Explanation is made below on each Example and each Comparative Example, based on the results obtained above.

          In Example 1, the porous substrate had a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 50 and the sol for membrane formation had a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 95  
15 and a  $\text{NaO}_2/\text{Al}_2\text{O}_3$  of 6.3, and all of the above requirements (1) to (3) for production of a laminated zeolite composite exhibiting excellent separation characteristic are satisfied. In Example 2, the porous substrate had a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 50 and the sol for membrane formation had a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 95 and a  
20  $\text{NaO}_2/\text{Al}_2\text{O}_3$  of 12.6, and all of the above requirements (1) to (3) for production of a laminated zeolite composite exhibiting excellent separation characteristic are satisfied.

          Meanwhile, in Comparative Examples 1 to 4, the porous substrate B having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of >400 was used and the  
25 requirement (1) is not satisfied. Further, in Comparative Example 1, a sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of >150 was used and the requirement (2) is not satisfied. In Comparative Example 3, a sol for membrane formation having a  $\text{NaO}_2/\text{Al}_2\text{O}_3$  of 18.9 was used and the requirement (3) is not  
30 satisfied.

In Comparative Examples 5 and 6, the porous substrate A having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 50 was used and the requirement (1) is satisfied. However, in Comparative Example 5, a sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of  $>150$  was used and the requirement (2) is not satisfied and, in Comparative Example 6, a sol for membrane formation having a  $\text{NaO}_2/\text{Al}_2\text{O}_3$  of 18.9 was used and the requirement (3) is not satisfied.

It is clear from the results of Table 3 and Fig. 1 that Examples 1 and 2, compared with Comparative Examples 1 to 6, each show a very high separation factor for n-butane and isobutane. That is, it is clear that the laminated zeolite composites of Examples 1 and 2, as compared with those of Comparative Examples 1 to 6, each have excellent separation characteristic and hardly generate inconveniences such as cracks on MFI membrane.

Incidentally, the laminated zeolite composites of Examples 1 and 2, as compared with those of Comparative Examples 1 to 6, showed a high separation factor of about 1.5 times, also in separation of propane and propylene.

#### Industrial Applicability

As described above, in the laminated zeolite composite of the present invention, the MFI membrane and the porous substrate each have a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of given range and the MFI membrane is formed in a given thickness on such a porous substrate. Therefore, the present laminated zeolite composite has high separation characteristic and high permeability and can be suitably used in, for example, separation of butane isomers or of propane and propylene.

According to the present method for producing a

laminated zeolite composite, since a porous substrate having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of given range is immersed in a sol for membrane formation having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of given range, the MFI membrane formed can easily have a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of predetermined range.